Video Article

Synthesis of High Purity Nonsymmetric Dialkylphosphinic Acid Extractants

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Abstract

We present the synthesis of (2,3-dimethylbutyl)(2,4,4'-trimethylpentyl)phosphinic acid as an example to demonstrate a method for the synthesis of high purity nonsymmetric dialkylphosphinic acid extractants. Low toxic sodium hypophosphite was chosen as the phosphorus source to react with olefin A (2,3-dimethyl-1-butene) to generate a monoalkylphosphinic acid intermediate. Amantadine was adopted to remove the dialkylphosphinic acid byproduct, as only the monoalkylphosphinic acid can react with amantadine to form an amantadine·mono-alkylphosphinic acid salt, while the dialkylphosphinic acid cannot react with amantadine due to its large steric hindrance. The purified monoalkylphosphinic acid was then reacted with olefin B (diisobutylene) to yield nonsymmetric dialkylphosphinic acid (NSDAPA). The unreacted monoalkylphosphinic acid can be easily removed by a simple base-acid post-treatment and other organic impurities can be separated out through the precipitation of the cobalt salt. The structure of the (2,3-dimethylbutyl)(2,4,4'-trimethylpentyl)phosphinic acid was confirmed by ^{31}P NMR, ^{1}H NMR, ESI-MS, and FT-IR. The purity was determined by a potentiometric titration method, and the results indicate that the purity can exceed 96%.

Video Link

The video component of this article can be found at https://www.jove.com/video/56156/

Introduction

Acidic organophosphorus extractants are widely used in the traditional hydrometallurgy field for extraction and separation of rare earth ions[1,2], non-ferrous metals (like Co/Ni[3,4]), rare metals (such as Hf/Zr[5], V[6,7]), actinides[8], *etc*. In recent years, they have also attracted more attention in the fields of secondary resource recycling and high-level liquid waste disposal[9]. Di-(2-ethylhexyl)phosphoric acid (D2EHPA or P204), 2-ethylhexylphosphoric acid mono-2-ethylhexyl ester (EHEHPA, PC 88A, or P507), and Di-(2,4,4'-trimethylpentyl)-phosphinic acid (Cyanex272), which are representatives of dialkylphosphoric acids, alkylphosphoric acid mono-alkyl esters, and dialkylphosphinic acids respectively, are the most commonly used extractants. Their acidity decreases in the following sequence: P204 > P507 > Cyanex 272. The corresponding extraction ability, extraction capacity, and stripping acidity are all in the order of P204 > P507 > Cyanex 272, and the separation performance is in the opposite order. These three extractants are effective in most cases. However, there are still some conditions where they are not so efficient: in heavy rare earths separation, of which the existing main problems are the poor selectivity and high stripping acidity for P204 and P507, low extraction capacity, and emulsion tendency during extraction for Cyanex 272. Thus, the development of novel extractants has drawn greater attention in recent years.

The class of dialkylphosphinic acid extractants is considered to be one of the most important research aspects to develop new extractants. Recent research showed that the extraction ability of dialkylphosphinic acids depends largely on the structure of the alkyl substituent[10,11]. It can be a wide range from significantly higher than that of P507 to lower than that of Cyanex 272[12]. However, the exploration of novel dialkylphosphinic acid extractants is restricted to the commercial olefin structure[10,12,13,14,15,16]. Though dialkylphosphinic acid extractants can also be synthesized by the Grignard-reaction method, the reaction conditions are rigorous[12,17].

NSDAPA, of which the two alkyls are different, opens a door to the exploration of new extractants. It makes the structures of dialkylphosphinic acid more diverse, and its extraction and separation performance can be fine-tuned by modifying both of its alkyl structures. The traditional synthetic method of NSDAPA used PH_3 as a phosphorus source, which has many drawbacks like high toxicity, rigorous reaction conditions, and difficult purification. Recently we reported a new method to synthesize NSDAPA using sodium hypophosphite as a phosphorus source (see **Figure 1**) and successfully synthesized three NSDAPAs[18]. This detailed protocol can help new practitioners repeat the experiments and master the synthetic method of NSDAPA extractants. We take (2,3-dimethylbutyl)(2,4,4'-trimethylpentyl)phosphinic acid as an example. The names and structures of olefin A, the mono-alkylphosphinic acid intermediate, olefin B, and the corresponding NSDAPA are shown in **Table 1**.

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Protocol

1. Synthesis of Mono-(2,3-dimethylbutyl)phosphinic acid [18,19]

1. **Reaction**
    1. Weigh 31.80 g sodium hypophosphite hydrate, 16.00 g acetic acid, 8.42 g 2,3-dimethyl-1-butene, 0.73 g di-*tert*-butylnperoxide (DTBP), and 25.00 g tetrahydrofuran (THF) into a 100 mL Teflon-lined stainless steel autoclave, put a magnetic stirrer into the autoclave, and seal it.
    2. Put the autoclave in a vertical tube furnace under which is a magnetic stirringapparatus.Start the magnetic stirring apparatus and set the speed at 800 rpm.
    3. Set the heating program of the temperature controller connected to the autoclave: heat from room temperature to 120 °C during 90 min, maintain at 120 °C for 8 h, then cool down to room temperature naturally. Start the heating program.

2. **Post-treatment**
    1. Transfer the products into a 250 mL one-neck round-bottom flask, wash the Teflon-lining with 50 mL THF, and add it into the same flask to ensure that all the products are transferred.
    2. Remove the THF and unreacted olefins using a rotary evaporator.
    3. Transfer the residua into a 250 mL separating funnel, wash the flask with 80 mL ethyl ether and 30 mL deionized water respectively, and add them into the same separating funnel to ensure that all the products are transferred.
    4. Add 50 mL 4% NaOH solution into the above separating funnel, shake it vigorously, and separate the aqueous phase. Extract the organic phase with 20 mL 4% NaOH solutions for three times (20 mL × 3) to ensure that the aqueous phase exceeds pH 10.
    5. Combine the aqueous solutions in the above step, and transfer them into a 500 mL separating funnel.
    6. Add 90 mL of 10% H_2SO_4 solution and 50 mL of ethyl ether, shake vigorously, and separate the organic phase; then extract the aqueous phase with 30 mL of ethyl ether for three times (30 mL × 3).
    7. Combine the ethyl ether solutions in step 1.2.6, and transfer them into another 500 mL separating funnel.
    8. Wash it with 100 mL of saturated NaCl solutions four times (100 mL × 4).
    9. Add 4 g of anhydrous $MgSO_4$ to remove any soluble water. Filter to remove the solid, and collect the liquid in a clean 250 mL one-neck round-bottom flask.
    10. Remove the ethyl ether using the rotary evaporator to obtain 17.92 g of the crude product.

2. Purification of Mono-(2,3-dimethylbutyl)phosphinic Acid

1. **Preparation of amantadine solution**
    1. Dissolve 22.28 g of amantadine hydrochloride in 100 mL of deionized water in a 500 mL beaker.
    2. Add 100 mL of saturated NaOH solution, and stir for 5 min.
    3. Add 150 mL of ethyl ether, and stir until the white precipitate generated in step 2.1.2 disappears.
    4. Transfer the solutions into a 500 mL separating funnel, wash the beaker with ethyl ether for three times (50 mL × 3), and combine them into the same separating funnel.
    5. Separate the aqueous phase, and wash the organic phase with saturated NaCl solutions five times (100 mL × 5).
    6. Add 4 g of anhydrous $MgSO_4$ to remove any soluble water. Filter to obtain the amantadine ethyl ether solution.

2. **Preparation of amantadine · mono-(2,3-dimethylbutyl)phosphinic acid salt**
    1. Add drop-wise the crude mono-(2,3-dimethylbutyl)phosphinic acid product to the amantadine solution. During dropping add 150 mL of ethyl ether to ensure that it can stir properly.
    2. Wash the one-neck round-bottom flask containing the mono-(2,3-dimethylbutyl)phosphinic acid product with 50 mL of ethyl ether to ensure that all the product is transferred to the amantadine solution. Stir for 30 min, and let it sit overnight.
    3. Filter under reduced pressure, and wash the filter cake with 200 mL ethyl ether.

3. **Release the mono-(2,3-dimethylbutyl)phosphinic acid**
    1. Transfer the filtered cake into a 500 mL beaker, add 80 mL of 1 M HCl, and stir for 5 min.
    2. Add 70 mL ethyl acetate, and stir for another 5 min.
    3. Transfer the solutions into a 250 mL separating funnel and separate the aqueous phase.
    4. Extract the aqueous phase with 40 mL ethyl acetate again and combine the ethyl acetate solutions.
    5. Wash the ethyl acetate solution with 30 mL of 1 M HCl twice (30 mL × 2) and saturated NaCl three times (80 mL × 3), sequentially.
    6. Add 4 g anhydrous $MgSO_4$ to remove any soluble water. Filter and collect the liquid in a 250 mL one-neck round-bottom flask.
    7. Remove the ethyl acetate using the rotary evaporator, and obtain 12.45 g of the pure mono-(2,3-dimethylbutyl)phosphinic acid (Yield: 82.9%).

3. Synthesis of (2,3-dimethylbutyl)(2,4,4'-trimethylpentyl)phosphinic Acid

1. **Reaction**
    1. Transfer all of the pure mono-(2,3-dimethylbutyl)phosphinic acid product into a 100 mL Teflon-lined stainless steel autoclave, add 4.95 g of acetic acid, 25.39 g of diisobutylene, 0.30 g of DTBP, put a magnetic stirrer into the autoclave, and seal it.
    2. Put the autoclave in a vertical tube furnace under which is a magnetic stirring apparatus, and start the magnetic stirring apparatus.

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3. Set the heating program of the temperature controller: heat from room temperature to 135 °C during 90 min, maintain at 135 °C for 8 h, then cool down to room temperature naturally. Start the heating program.
4. When the reaction system cools down to room temperature, add another 0.30 g of DTBP, and restart the heating program.
5. Repeat step 3.1.4 once.

2. **Post-treatment**
   1. Dilute the product with 100 mL ethyl ether, and then transfer to a 250 mL separating funnel.
   2. Wash it with 30 mL of 4% NaOH three times (30 mL × 3) to ensure that aqueous phase exceeds pH 10.
   3. Add 70 mL of 10% H_2SO_4 solution to acidify the product.
   4. Wash it with saturated NaCl solution several times (80 mL each) until the aqueous phase pH equals pH 6-7.
   5. Add 4 g of anhydrous $MgSO_4$ to remove any soluble water. Filter to remove the solid, and collect the liquid in a clean 250 mL one-neck round-bottom flask.
   6. Remove the ethyl ether and unreacted olefins using the rotary evaporator to obtain 15.10 g of crude product.

4. Purification of (2,3-dimethylbutyl)(2,4,4'-trimethylpentyl)phosphinic Acid

1. **Obtain pure co-(2,3-dimethylbutyl)(2,4,4'-trimethylpentyl)phosphinic acid complex**
   1. Dissolve 2.30 g of NaOH in 40 mL deionized water. Add the NaOH solution to the flask containing the crude (2,3-dimethylbutyl)(2,4,4'-trimethylpentyl)phosphinic acid product, and shake it vigorously for 5 min.
   2. Add 0.5 M $CoCl_2$ solution dropwise while shaking until no more blue precipitate is generated and the solution in the flask is pink.
   3. Filter and wash the blue precipitate with deionized water until the filter cake is colorless.
   4. Transfer the filter cake into a 250 mL beaker, add 100 mL of acetone, seal it with preservative film, and then refrigerate it at 4 °C for one night.
   5. Pulverize the blue precipitate to release any impurities trapped in the bulk.
   6. Filter and wash it with 100 mL of fresh acetone. Dry the filter cake at room temperature, and then transfer it into a 250 mL separating funnel.

2. **Regenerate the (2,3-dimethylbutyl)(2,4,4'-trimethylpentyl)phosphinic acid**
   1. Add 120 mL ethyl ether and 80 mL 10% H_2SO_4, and shake vigorously until the blue precipitate disappears.
   2. Separate the aqueous phase,wash the organic phase sequentially with 30 mL of 10% H_2SO_4 once and saturated NaCl solutions several times (80 mL each) until the aqueous phase pH equals pH 6-7.
   3. Add 4 g of anhydrous $MgSO_4$ to remove any soluble water. Filter to remove the solid and collect the liquid in a clean 250 mL one-neck round-bottom flask.
   4. Remove the ethyl ether using the rotary evaporator, and obtain 11.46 g of the pure product (Yield: 52.8%).

Representative Results

^{31}P NMR spectra were collected for the mono-(2,3-dimethylbutyl)phosphinic acid before and after purification by the amantadine method (**Figure 1a-b**). ^{31}P NMR spectra, ^{1}H NMR spectra, MS spectra, and FT-IR spectra were collected for (2,3-dimethylbutyl)(2,4,4'-trimethylpentyl)phosphinic acid (see **Figure 3**, **Figure 4**, **Figure 5**, and **Figure 6**, respectively) after purification by a cobalt salt precipitation method. Potentiometric titration curves of (2,3-dimethylbutyl)(2,4,4'-trimethylpentyl)phosphinic acid were recorded (**Figure 7**)[19].

During the mono-alkylphosphinic acid synthesis, it is difficult to avoid the generation of corresponding dialkylphosphinic acid byproduct (see **Figure 1a**), which cannot be removed by the base-acid post-treatment. That is the reason for the absorption peak (62.507 ppm) of di-(2,3-dimethylbutyl)phosphinic acid in **Figure 2a**. When olefin A was 1-octene or cyclohexene, similar phenomena occurred[18]. 2,4-dimethyl-1-heptene, which contains nine carbon atoms, was also tested but the same phenomena also occurred. **Figure 2b** shows the ^{31}P NMR spectra of pure mono-(2,3-dimethylbutyl)phosphinic acid.

Structural characterization of the (2,3-dimethylbutyl)(2,4,4'-trimethylpentyl)phosphinic acid:
^{31}P NMR (243 MHz, $CDCl_3$) δ (**Figure 3**): 61.40(s). ^{1}H NMR (600 MHz, $CDCl_3$) δ (**Figure 4**): 0.82-0.88 (m, 6H, $2CH_3$), 0.92 (s, 9H, $3CH_3$), 1.01-1.04 (m, 3H, CH_3), 1.12-1.15 (m, 3H, CH_3), 1.15-1.21 (m, 1H), 1.32-1.38 (m, 1H), 1.41-1.49 (m, 1H), 1.51-1.60 (m, 1H), 1.61-1.78 (m, 3H), 1.87-1.95 (m, 1H), 2.04-.14 (m, 1H), 11.862 (s, 1H, OH).

ESI-MS (+) m/z (**Figure 5a**): 263 $[M+H]^+$, 304 $[M+C_3H_6]^+$, 525 $[2M+H]^+$, 547 $[2M+Na]^+$, 567 $[2M+C_3H_7]^+$. ESI-MS (-) m/z (**Figure 5b**): 261 $[M-H]^-$, 523 $[2M-H]^-$, 566 $[2M+C_3H_7-H]^-$. FT-IR wavenumbers (cm^{-1}) (**Figure 6**): 2876.55-2902.84 C-H stretching, 2619.51 O-H stretching caused by dimer formation, 1667.29 O-H bending, 1467.91 C-H bending, 1366.13 C-H rocking, 1237.41 C-C stretching of the tert-butyl group, 1165.57 P=O stretching, 962.69 P-O(H) stretching, 821.97 P-C stretching. The relevant vibrational characteristic bands are similar to those of phosphonic acids, phosphoric acids, and other phosphinic acids[20,21].

The ^{31}P and ^{1}H NMR spectra, ESI-MS spectra, and FT-IR spectrum confirmed the structure of (2,3-dimethylbutyl)(2,4,4'-trimethylpentyl)phosphinic acid. The potentiometric titration results (**Figure 7**[19]) indicate that the purity of the final product can exceed 96%.

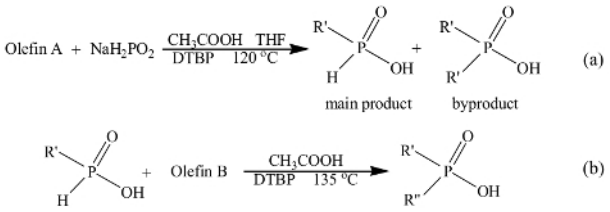

Figure 1. Synthesis route of NSDAPA acids. Please click here to view a larger version of this figure.

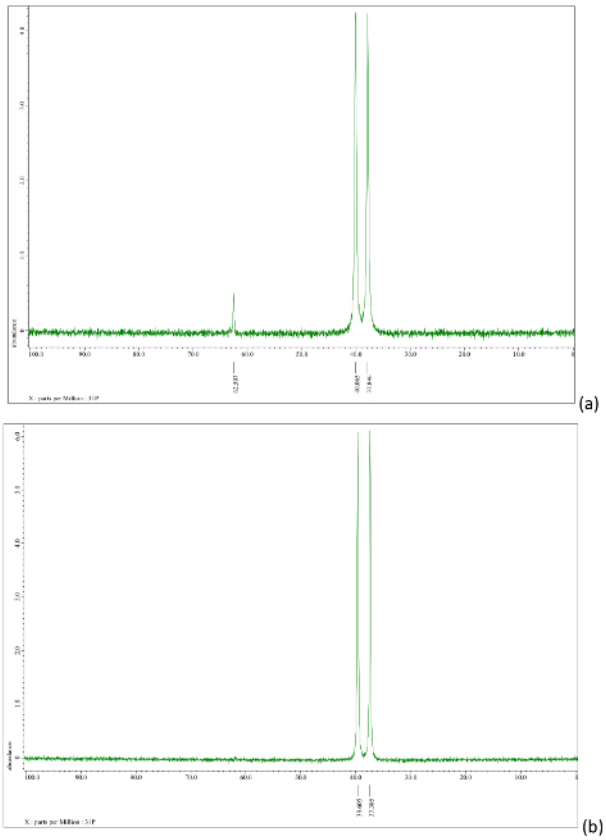

Figure 2.^{31}P NMR spectra (243 MHz, $CDCl_3$) of mono-(2,3-dimethylbutyl)phosphinic acid (**a**) before and (**b**) after purification by the amantadine method. Please click here to view a larger version of this figure.

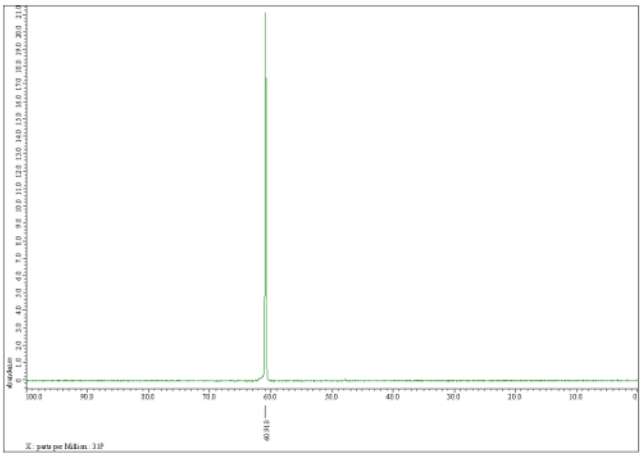

Figure 3.^{31}P NMR spectrum (243 MHz, $CDCl_3$) of (2,3-dimethylbutyl)(2,4,4'-trimethylpentyl)phosphinic acid after purification by the cobalt salt precipitation method. Please click here to view a larger version of this figure.

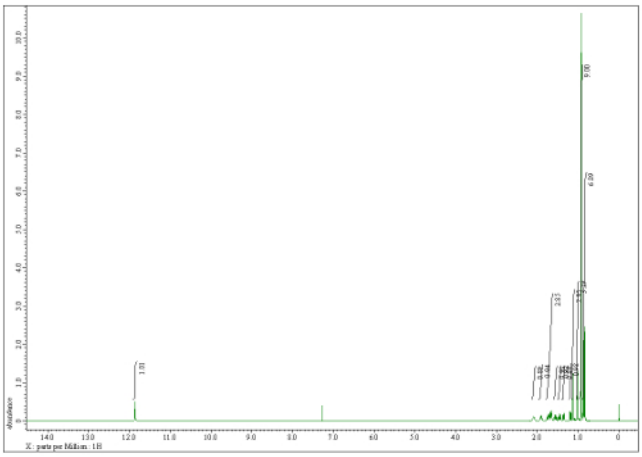

Figure 4. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of (2,3-dimethylbutyl)(2,4,4'-trimethylpentyl)phosphinic acid after purification by the cobalt salt precipitation method. Please click here to view a larger version of this figure.

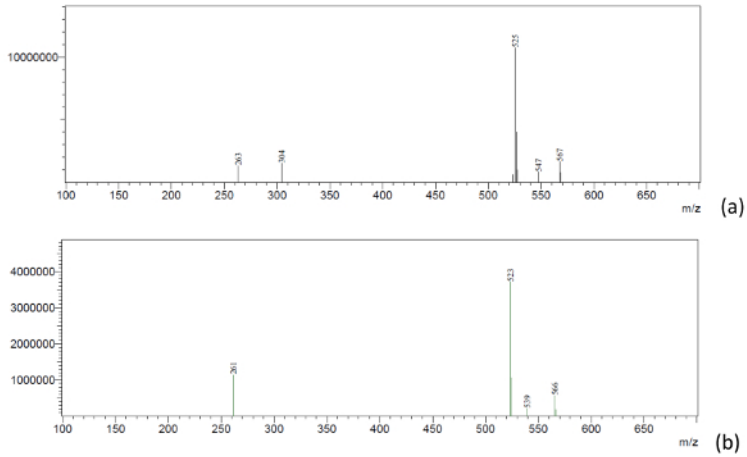

Figure 5. ESI-MS spectra of (2,3-dimethylbutyl)(2,4,4'-trimethylpentyl)phosphinic acid after purification by cobalt salt precipitation method, (**a**) Positive and (**b**) Negative. Please click here to view a larger version of this figure.

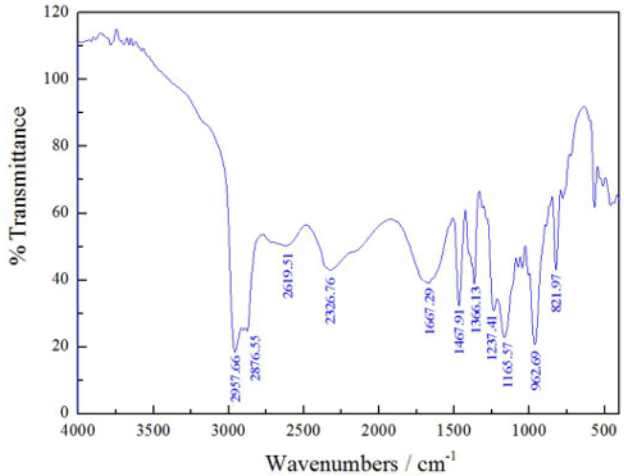

Figure 6. FT-IR spectrum of pure (2,3-dimethylbutyl)(2,4,4'-trimethylpentyl)phosphinic acid after purification by the cobalt salt precipitation method. Please click here to view a larger version of this figure.

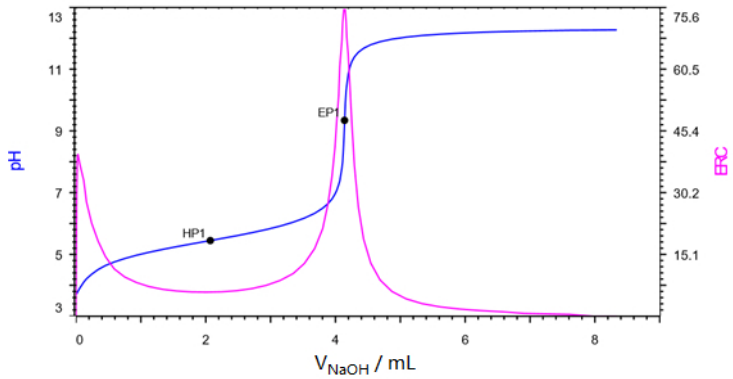

Figure 7. Potentiometric titration curve of (2,3-dimethylbutyl)(2,4,4'-trimethylpentyl)phosphinic acid (m = 0.1270 g) in 75% alcohol (v/v) with 0.1127 mol/L NaOH. Please click here to view a larger version of this figure.

Discussion

The most critical step within the protocol is the mono-alkylphosphinic acid synthesis (**Figure 1a**). In this reaction, a higher yield and less dialkylphosphinic acid by-product is better. Increasing the molar ratio of NaH_2PO_2/olefin A will improve the yield and inhibit the generation of dialkylphosphinic acid by-product. However, a large NaH_2PO_2 dosage will also increase the cost and cause a stirring problem. The preferred molar ratio of NaH_2PO_2/olefin A is 3:1. As a solvent, THF is better than *n*-octane, 1,4-dioxane, and cyclohexane in this reaction. As to the initiator, DTBP is better than 2,2-azobisisobutyronitrile (AIBN)[18]. To separate the mono-alkylphosphinic acid from the di-alkylphosphinic acid by-product, the amantadine method can be adopted. The mono-alkylphosphinic acid can react with amantadine to generate a white precipitation, while the di-alkylphosphinic acid cannot due to its large spatial restrictions and it still remains in the organic solution. Separate the white precipitation by filtration, and add an inorganic strong acid (like HCl or H_2SO_4) to regenerate the mono-alkylphosphinic acid, so that complete separation of the mono-alkylphosphinic acid and di-alkylphosphinic acid by-product can be realized.

In the NSDAPA synthesis (**Figure 1b**), the molar ratio of olefin B/mono-alkylphosphinic acid is more than 1:1 (2:1-4:1 is preferred) and the excess olefin B plays the role of the solvent. Though the olefin B is in excess, the mono-alkylphosphinic acid cannot react completely. The unreacted mono-alkylphosphinic acid will enter into the aqueous phase from the organic phase when it reacts with a base (like NaOH or KOH), so it can be easily removed simply by the base-acid post-treatment. During the base-acid post-treatment, the NSDAPA always remains in the organic phase, and thus its crude product always contains organic impurities such as unreacted olefin B, free radical fragments, oligomers, *etc*. These organic impurities are soluble in acetone, while the solubility of Co-NSDAPA complex is very small in icy acetone. This difference offers a way to further purify NSDAPA: react the NSDAPA with Co^{2+} to form a Co-NSDAPA complex, wash the complex with icy acetone to remove the organic impurities, and then add strong acid (like H_2SO_4 or HCl) to the complex to regenerate the NSDAPA.

This protocol describes a universal method for NSDAPA synthesis and purification. Compared with the traditional NSDAPA synthetic method with PH_3 as the phosphorus source, our method has the advantages of low toxicity, mild reaction conditions, easy purification, and potential for large-scale production. This method offers a way to finely adjust the performance of dialkylphosphinic acids. Like other organophosphorus acid extractants such as P204, P507, and Cyanex 272, NSDAPA can also be used in hydrometallurgy filed for extraction and separation of rare earth ions, non-ferrous metals, rare metals, actinides, *etc*. Our synthetic method of NSDAPA makes it possible to explore a number of potential separation systems with this class of extractants.

Disclosures

The authors have nothing to disclose.

Acknowledgements

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References

1. Swain, B., Otu, E.O. Competitive extraction of lanthanides by solvent extraction using Cyanex 272: Analysis, classification and mechanism. *Sep Purif Technol.* **83**, 82-90 (2011).
2. Wang, Y. L., *et al.* The novel extraction process based on CYANEX (R) 572 for separating heavy rare earths from ion-adsorbed deposit. *Sep Purif Technol.* **151**, 303-308 (2015).
3. Regel-Rosocka, M., Staszak, K., Wieszczycka, K., Masalska, A. Removal of cobalt(II) and zinc(II) from sulphate solutions by means of extraction with sodium bis(2,4,4-trimethylpentyl)phosphinate (Na-Cyanex 272). *Clean Technol Envir.* **18**(6), 1961-1970 (2016).
4. Hereijgers, J., *et al.* Separation of Co(II)/Ni(II) with Cyanex 272 using a flat membrane microcontactor: Stripping kinetics study, upscaling and continuous operation. *Chem Eng Res Des.* **111**, 305-315 (2016).

5. Lee, M. S., Banda,R., Min, S.H. Separation of Hf(IV)-Zr(IV) in H_2SO_4 solutions using solvent extraction with D2EHPA or Cyanex 272 at different reagent and metal ion concentrations. *Hydrometallurgy.* **152**, 84-90 (2015).
6. Noori, M., Rashchi, F., Babakhani, A., Vahidi, E. Selective recovery and separation of nickel and vanadium in sulfate media using mixtures of D2EHPA and Cyanex 272. *Sep Purif Technol.* **136**, 265-273 (2014).
7. Li, X. B., *et al.* Thermodynamics and mechanism of vanadium(IV) extraction from sulphate medium with D2EHPA, EHEHPA and CYANEX 272 in kerosene. *Trans Nonferrous Met Soc China.* **22**(2), 461-466 (2012).
8. Das, D., *et al.* Effect of the nature of organophosphorous acid moiety on co-extraction of U(VI) and mineral acid from aqueous solutions using D2EHPA, PC88A and Cyanex 272. *Hydrometallurgy.* **152**, 129-138 (2015).
9. Baba, A. A., *et al.* Extraction of copper from leach liquor of metallic component in discarded cell phone by Cyanex (R) 272. *JESTEC.* **11**(6), 861-871 (2016).
10. Du, R. B., *et al.* Microwave-assisted synthesis of dialkylphosphinic acids and a structure-reactivity study in rare earth metal extraction. *RSC Adv.* **5**(126), 104258-104262 (2015).
11. Du, R. B., *et al.* alpha, beta-Substituent effect of dialkylphosphinic acids on anthanide extraction. *RSC Adv.* **6**(61), 56004-56008 (2016).
12. Wang, J. L., Xu, S. X., Li, L. Y., Li, J. Synthesis of organic phosphinic acids and studies on the relationship between their structure and extraction-separation performance of heavy rare earths from HNO_3 solutions. *Hydrometallurgy.* **137**, 108-114 (2013).
13. Hino, A., Nishihama, S., Hirai, T., Komasawa, I. Practical study of liquid-liquid extraction process for separation of rare earth elements with bis (2-ethylhexyl) phosphinic acid. *J Chem Eng Jpn.* **30**(6), 1040-1046 (1997).
14. Ju, Z. J., *et al.*Synthesis and extraction performance of di-decylphosphinic acid. *Chin J Nonferrous Met.* **20**(11), 2254-2259 (2010).
15. Li, L. Y., *et al.* Dialkyl phosphinic acids: Synthesis and applications as extractant for nickel and cobalt separation. *Trans Nonferrous Met Soc China.* **20**, 205-210 (2010).
16. Wang, J. L., *et al.* Solvent extraction of rare earth ions from nitrate media with new extractant di-(2,3-dimethylbutyl)-phosphinic acid. *J Rare Earths.* **34**(7), 724-730 (2016).
17. Hu, W.X. Synthesis and properties of di-tertiary alkylphosphinic acids. *Chem J Chin Univ-Chin.* **15**(6), 849-853 (1994).
18. Wang, J. L., Chen, G., Xu, S. M., Li, L. Y. Synthesis of novel nonsymmetric dialkylphosphinic acid extractants and studies on their extraction-separation performance for heavy rare earths. *Hydrometallurgy.* **154**, 129-136 (2015).
19. Wang, J. L., Xie, M. Y., Wang, H. J., Xu, S. M. Solvent extraction and separation of heavy rare earths from chloride media using nonsymmetric (2,3-dimethylbutyl)(2,4,4′-trimethylpentyl)phosphinic acid. *Hydrometallurgy.* **167**, 39-47 (2017).
20. Menoyo, B., Elizalde, M. P., Almela, A. Determination of the degradation compounds formed by the oxidation of thiophosphinic acids and phosphine sulfides with nitric acid. *Anal Sci.* **18**(7), 799-804 (2002).
21. Darvishi, D., *et al.* Synergistic effect of Cyanex 272 and Cyanex 302 on separation of cobalt and nickel by D2EHPA. *Hydrometallurgy.* **77**, 227-238 (2005).

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